

REMARKS

Claim 1 has been amended to incorporate therein the recitation of claim 3 (to recite that the wiring board is obtained by coating a copper paste comprising a copper powder, an organic vehicle and an Fe_2O_3 particle as a conductor layer on a ceramic green sheet) and simultaneously firing the ceramic green sheet and coated copper paste. Support is found, for example, at page 1, lines 6-9 of the specification.

Claim 3 has been canceled. Claims 4, 5 and 6 have been amended to depend from claim 1. Claim 6 has been further amended to conform with the amendment to claim 1.

Entry of the amendments and review and reconsideration on the merits are respectfully requested.

Claims 1-4 and 6-9 stand rejected; and claim 5 is objected to as being allowable if rewritten in independent form.

Claim 7 was rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 5,468,445 to Casey et al. Casey et al. was cited as disclosing a copper paste comprising copper powder, an organic vehicle and an Fe_2O_3 particle.

Applicants respectfully traverse for the following reasons.

Casey et al. discloses a Cu/Fe via paste containing Cu powder, Fe particle and ethyl cellulose binder (i.e., an organic vehicle). The Fe component different from an Fe_2O_3 particle is an "oxidizable second metal" incorporated into the copper-containing via paste to control copper shrinkage as well as to enhance adhesion (column 5, lines 66-column 6, line 1). Oxidation of iron to Fe_3O_4 or Fe_2O_3 results in volume expansion (column 6, lines 1-3), which oxidation occurs

when the substrate is sintered. See column 7, lines 15-20 and 30-33. The final composition of the via after sintering is Cu, Cu₂O and Fe₃O₄ (i.e., the Fe₂O₃ is further converted to Fe₃O₄ when the furnace is ramped to a higher temperature - see equation 2) at column 6. In any event, once the via paste is sintered resulting in conversion of Fe to iron oxide, the organic binder is also burned off.

Thus, when in paste form (prior to sintering), the copper-containing via paste of Casey et al. contains Fe but no Fe₂O₃ particle as required by claim 7. After sintering, the resulting via is no longer a paste as required by claim 7. Additionally, the sintered via no longer contains an organic vehicle as required by claim 7 because it is burned off at high temperature.

For the above reasons, it is respectfully submitted that claim 7 is not anticipated by Casey et al., and withdrawal of the foregoing rejection under 35 U.S.C. § 102(b) is respectfully requested.

Claim 8 was rejected under 35 U.S.C. § 103(a) as being unpatentable over Casey et al. The Examiner considered that it would have been within the level of ordinary skill to formulate a paste containing more than 20 parts by mass of organic vehicle.

Applicants rely on the response above with respect to the rejection of claim 7 over Casey et al. As shown above, the copper paste of Casey et al. does not contain an Fe₂O₃ particle as required by claim 7.

Withdrawal of the foregoing rejection under 35 U.S.C. § 103(a) is respectfully requested.

Claims 1 and 2 were rejected under 35 U.S.C. § 103(a) as being unpatentable over U.S. Patent 6,132,543 to Mohri et al. in view of JP 63-131405 (JP '405).

Mohri et al. was cited as disclosing a wiring board including a conductor layer and at least one of a radiator, etc., connected to the conductor layer through a joining member. Mohri et al. is said to generally teach that the conductor layer is a copper paste. The Examiner relied on JP '405 as teaching a copper paste containing copper and iron oxide. The reason for rejection was that it would have been obvious to use the copper paste of JP '405 in the wiring board of Mohri et al. to provide good wettability to solder and bonding strength.

Applicants traverse, and respectfully request the Examiner to reconsider in view of the amendment to claim 1 and the following remarks.

The present invention relates to the improvement of plating and soldering properties and the prevention of bulging (page 4, line 20 to page 5, line 3 of the specification) during brazing with respect to a conductive layer of a wiring board including a Cu wiring obtained by simultaneous firing (page 1, lines 6 to 14 of the specification). In particular, such technique is useful for connecting with a brazing material having a melting point of 270°C or higher (particularly, 300°C or higher) (page 14, lines 13 to 25).

Mohri et al. describes a soldering connection for a wiring board, but is silent as to a wiring board including a Cu wiring obtained by simultaneous firing, and thus has no description of the problem of bulging during brazing associated with simultaneous firing treated by the present invention. The Examiner cites Mohri et al. as describing a Cu paste (column 9, lines 50 to 55), but this passage relates to firing a Cu paste on a fired board, not to a wiring board including a Cu wiring obtained by simultaneous firing of a ceramic green sheet and coated copper paste.

JP '405 (translation enclosed) describes the enhancement of adhesive strength by incorporating FeO into a Cu paste. However, the Cu paste in JP '405 is printed and fired on a ceramic board (not a green sheet) to provide a Cu conductor thereon (see [Industrial field of application] at page 2). Thus, there is no description in JP '405 of a wiring board including Cu wiring obtained by simultaneous firing. Moreover, JP '405 emphasizes adhesive strength, insisting that, in addition to FeO, incorporation of Cu_2O , NiO, etc., is also effective. Suppression of bulging during brazing, which is the problem at issue, cannot be solved by enhancing adhesive strength alone (page 22, lines 13 to 18 of the specification). The present inventors found that incorporation of Fe_2O_3 is specifically effective for solving this problem.

Moreover, claim 1 has been amended to incorporate therein the recitation of claim 3 which was not rejected over Mohri et al. in view of JP '405.

For the above reasons, it is respectfully submitted that claims 1 and 2 are patentable over Mohri et al. in view of JP '405, and withdrawal of the foregoing rejection under 35 U.S.C. § 103(a) is respectfully requested.

Claims 1, 3 and 6 were rejected under 35 U.S.C. § 103(a) as being unpatentable over Mohri et al. in view of Casey et al.

Applicants respectfully traverse for the following reasons.

Casey et al. describes that Fe is incorporated into a Cu paste. However, Casey et al.'s technique, which relates to preparation of a via, involves dissolving a gap that is formed between the via and a ceramic (column 3, lines 17 to 20). This gap problem is solved by oxidative swelling of the metal, as well as oxidation of Cu through incorporation of an oxidizable metal.

For that purpose, Casey et al. describes that Ni and Co are also effective in addition to Fe as an oxidizable metal (column 8, lines 12 to 18).

On the other hand, the conductive layer of the present invention, which is a surface conductive layer formed by coating a specific copper paste on a ceramic green sheet and simultaneously firing the same, is different from a via which vertically extends through stacked layers. Thus, oxidative swelling of a metal cannot suppress bulging during brazing which is the problem addressed by the present invention. Additionally, suppression of bulging during brazing cannot be achieved by enhancing adhesive strength alone, namely, by introducing copper oxide (page 22, lines 13 to 18 of the specification). To solve this problem, the present inventors found that incorporating Fe_2O_3 is specifically effective.

To more clearly distinguish the invention over the cited prior art, claim 1 has been amended to recite that the wiring board is obtained by coating a copper paste comprising a copper powder, an organic vehicle and an Fe_2O_3 particle as a conductor layer on a ceramic green sheet, and simultaneously firing the ceramic green sheet and coated copper paste. As discussed above, the cited prior art does not simultaneously fire the ceramic green sheet and coated copper paste, and therefore does not recognize the problem of bulging during brazing specific to simultaneously fired wiring boards. One of ordinary skill could never arrive at the present invention based on the teachings of Mohri et al. and Casey et al. which do not concern simultaneously fired wiring boards. For the above reasons, and in view of the amendment to claim 1, it is respectfully submitted that claims 1 and 6 are patentable over Mohri et al. in view of Casey et al., and withdrawal of the foregoing rejection under 35 U.S.C. § 103(a) is respectfully requested.

Claims 7 and 9 were rejected under the judicially created doctrine of obviousness-type double patenting as being unpatentable over claim 18 of U.S. Patent 6,855,399 (US '399).

In response, the common Assignee submits herewith a Terminal Disclaimer disclaiming the terminal part of any patent granted on the above-identified Application No. 10/620,361 which would extend beyond the expiration of the full statutory term as presently shortened by any Terminal Disclaimer of U.S. Patent 6,855,399. Withdrawal of the foregoing obviousness-type double patenting rejection is respectfully requested.

Withdrawal of all rejections and allowance of claims 1, 2 and 4-9 is earnestly solicited.

In the event that the Examiner believes that it may be helpful to advance the prosecution of this application, the Examiner is invited to contact the undersigned at the local Washington, D.C. telephone number indicated below.

The USPTO is directed and authorized to charge all required fees, except for the Issue Fee and the Publication Fee, to Deposit Account No. 19-4880. Please also credit any overpayments to said Deposit Account.

Respectfully submitted,



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23373

CUSTOMER NUMBER

Date: June 20, 2005

JP-A-63-131405

Specification

1. Title of the Invention

Composition for conductor

2. Scope of the Claim for Patent

(1) A composition for a conductor, essentially comprising from 80 to 92% by weight of a Cu powder, from 0.5 to 8 % by weight of a glass powder, from 0.01 to 4.5% by weight of a lower oxide of a polyvalent metal, from 0 to 1% by weight of an inorganic nonoxide and from 5 to 20% by weight of an organic binder.

(2) The composition according to claim 1, wherein the lower oxide is at least one member selected from FeO, MnO, V₂O₃, Cr₂O₃, CeO₂, Sb₂O₃, As₂O₃, NiO, SnO and Cu₂O.

(3) The composition according to claim 2, wherein the nonoxide is at least one member selected from Cr, W, ZrB₂ and SiC.

(4) The composition according to claim 1 or 3, wherein the glass powder comprises:

PbO	45 to 85
SiO ₂	20 to 40
Al ₂ O ₃	0.1 to 5
B ₂ O ₃	0 to 8
R ₂ O	0 to 3

(R is at least one member out of Li, Na and K),

ZnO 0 to 10 and

TiO₂+SnO₂ 0 to 5

(expressed in percent by weight).

(5) The composition according to claim 1 or 4, wherein the lower oxide and the lower oxide comprise:

Cr₂O₃ 0.1 to 3

V₂O₃ 0.005 to 0.3 and

W 0 to 0.18

(expressed in percent by weight).

3. Detailed Description of the Invention

[Industrial Field of Application]

The present invention concerns a Cu conductor paste which is screen-printed on a substrate made of ceramics such as alumina, followed by drying/firing to form a Cu thick film conductor on the substrate.

[Prior Art]

A Cu conductor is ordinarily fired in an N₂ atmosphere containing from 1 to 10 ppm of oxygen for preventing oxidation, and is required for solder wettability, adhesion with a substrate and stability of sheet resistance and in addition, high reliability. With regard to those characteristics, existing commercially available products have been degraded in the solder wettability by refiring, or have lower adhesion strength than that of Ag-Pd conductor, thus there is no product

that satisfies all the characteristics.

[Means for Solving the Problems]

As described above, the disadvantages of the existing Cu past include low adhesion strength in initial characteristics, degradation of adhesion strength due to refire (firing in N₂, at 900°C for 10 min), degradation of solder wettability and further degradation of characteristics in reliability tests (for example, in a case of being left to stand at high-temperature of 150°C for 200 hours).

The invention has an aim to solve the problems involved in the existing pastes, and to provide a conductor paste composition having high adhesion strength with a substrate, and whose degradation of adhesion strength due to refiring and solder wettability is extremely reduced.

[Means for Solving the Problem]

The invention provides a composition for a conductor, essentially comprising from 80 to 92% by weight of a Cu powder, from 0.5 to 8 % by weight of a glass powder, from 0.01 to 4.5% by weight of a lower oxide of a polyvalent metal, from 0 to 1% by weight of an inorganic nonoxide and from 5 to 20% by weight of an organic binder.

The Cu powder according to the invention is a main component constituting the conductor, and when the amount

of the Cu powder is less than 80% by weight, the sheet resistance of the Cu thick film conductor is increased, which is not preferred.

On the other hand, when it is more than 92% by weight, the amount of the organic binder in the paste is excessively decreased, then the printability upon screen-printing is degraded, which is not preferred. Especially preferable range thereof is from 85 to 90% by weight.

Basically, the Cu powder is preferably spherical, since this can decrease the amount of the organic binder, increase the Cu concentration, and suppress the sheet resistance to low level. With regard to such spherical shape, so long as a powder has a ratio R/r which is a ratio of the maximum diameter R to the minimum diameter r is 1.5 or less, the powder is expected to have an effect substantially equal to that of a spherical powder.

Incidentally, when the average particle size of the Cu powder is smaller than $1\text{ }\mu\text{m}$, a large amount of the organic binder to impart paste characteristics suitable to screen printing is required, which is not preferred. On the other hand, when it is greater than $4\text{ }\mu\text{m}$, the denseness of the conductor is lowered to increase sheet resistance value, which is not preferred. The preferable range thereof is from 1 to $4\text{ }\mu\text{m}$.

The glass powder is a binder for adhering the Cu

powder to the substrate through firing, and when the amount thereof is less than 0.5% by weight, adhesion strength is lowered, while on the other hand, when it is more than 8% by weight, the sheet resistance value is increased, as well as the solder wettability is lowered, which is not preferred. More preferable range is from 83% to 88%.

When the particle size of the glass powder is too large or too small, it is not preferred since the sheet resistance value is increased, as well as the solder wettability is lowered. Preferably, the average particle size is within a range of from 2 to 4 μm .

With regard to the glass powder, when the softening point thereof is too low, it is not preferred since the solder wettability of the conductor is lowered, while on the other hand, when the softening point is too high, the flowability is lowered to increase the sheet resistance value, as well as the adhesion strength is lowered. Preferably, the softening point thereof determined depending on DTA characteristics is within a range of from 500 to 850°C.

Further, a glass powder having the characteristics described above and having a heat expansion coefficient of $80 \times 10^{-7}/^{\circ}\text{C}$ (average value at 25 to 400°C) or less is especially preferred. The reason is that the heat

expansion coefficient, when it is excessively greater than the value described above, becomes greater than that of the substrate made of ceramics such as alumina, and adhesion strength is lowered, which is not preferred.

As glass having such characteristics, those having following composition are preferred. That is, those comprise from 45 to 85% by weight of PbO , from 20 to 40% by weight of SiO_2 , from 0.1 to 5% by weight of Al_2O_3 , from 0 to 8% by weight of B_2O_3 , from 0 to 3% by weight of R_2O (R is one member out of Li , K and Na), from 0 to 10% by weight of ZnO , and from 0 to 5% by weight of TiO_2+SnO_2 .

PbO : When the amount thereof is less than 45%, the glass softening point becomes too high, and the adhesion strength is lowered. While on the other hand, when it is more than 85%, the softening point becomes too low, as well as the heat expansion coefficient

becomes too large which does not agree with that of the substrate, thus it is not preferred. The preferable amount thereof ranges from 47 to 63%.

SiO_2 : When the amount thereof is less than 20%, the heat expansion coefficient becomes too large to lower the adhesion strength. While on the other hand, when it is more than 40%, the softening point becomes too high to lower the adhesion strength. Preferable amount thereof ranges from 22 to 38%.

AlO_2 : When the amount thereof is less than 0.1%, it is not preferred since there is possibility of occurrence of devitrification during the glass melt-forming process. While on the other hand, when the amount is more than 5%, it is not preferred since the glass softening point become too high. The preferable range is from 0.5 to 4.5%.

B_2O_3 : Although it may be used as a flux component, when the amount thereof exceeds 8%, it is not preferred since the heat expansion is made too large.

R_2O (one member out of R-Li, Na, K):

In addition to the use thereof as a flux component, it is used with an aim of improving acid resistance of glass. When the amount is more than 3%, however, it is not preferred since the heat expansion coefficient becomes too large.

ZnO : In addition to the use thereof as a flux component, it can be used for chemical stabilization of glass. When the amount is 10% or more, however, it tends to be crystallized during the glass firing step and the adhesion strength is lowered due to the loss of the flowability, which is not preferred.

$\text{TnO}_2 + \text{SnO}_2$:

With an aim of improving chemical stability of glass, the amount may be 5% or less. When it is more

than 5%, however, the softening point of the glass becomes too high, which is not preferred.

The polyvalent lower oxide has an effect of preventing the surface of the Cu powder from being oxidized upon firing, and when the amount of such oxide is less than 0.01%, it is not preferred since the effect can not be provided sufficiently. While on the other hand, when the content exceeds 4.5%, it is not preferred since the sheet resistance is increased or adhesion strength with the substrate is lowered.

As such oxide, it is preferred to use FeO, MnO, V_2O_3 , Cr_2O_3 , CeO_2 , Sb_2O_3 , As_2O_3 , NiO, SnO, Cu_2O alone or two or more of them may be used in combination owing to their relatively easy availability and easy handling.

Addition of an inorganic nonoxide is not essential, however, the addition provides an effect of preventing the surface of Cu powder from being oxidized, similar to the oxide described above. When the content of such nonoxide exceeds 1% or more, however, it is not preferred since adhesion strength with the substrate is lowered. Those having especially excellent effects as such nonoxide include Cr, W, ZrB_2 and SiC, and they are used alone or two or more of them are used in combination.

Among those described above, an especially preferable combination of the polyvalent lower oxide and

the nonoxide is described below.

CrO_3	0.1 to 3
V_2O_3	0.005 to 0.3
W	0 to 0.10

The particle size of such oxide and nonoxide is, preferably, from 0.5 to 4 μm in average.

The organic binder is used for retaining the adhesion of the printed conductor to the substrate till the firing is carried out, and when the content thereof is less than 5%, the retainability is lowered, and when the content thereof is more than 20%, the Cu content is reduced, so that the film thickness after printing and firing is reduced to increase the sheet resistance, which is not preferred.

Such organic binder is not particularly restrictive, and ethylcellulose dissolved in a solvent such as α -terpineol, or the like is used.

In the composition according to the invention, the total amount of the components described above may be 94% or more, and with regard to the 6% of the balance, Bi_2O_3 , CuO , for example, are added, which can improve the adhesion.

[Function]

The effect of the lower oxide of a polyvalent metal and the effect of the nonoxide are recognized particularly

in the solder wettability. As a concept of the function, since the solder wettability is extremely worsened when those components are not used, it is considered that before occurrence of oxidation on the surface of the Cu powder, or even a part thereof is oxidized into Cu_2O or CuO , those components deprive oxygen in the atmosphere or oxygen on the Cu surface, thus occurrence of oxidation on the surface of the Cu surface is prevented.

[Example]

A Cu powder, a glass powder, a polyvalent metal lower oxide, an inorganic nonoxide and an organic binder were weighed, and kneaded.

The composition of the glass powder used was, expressed by percent by weight, $\text{PbO}(80)$, $\text{SiO}_2(33)$, $\text{Al}_2\text{O}_3(2)$, $\text{B}_2\text{O}_3(4)$, $\text{K}_2(0.5)$ and $\text{Na}_2\text{O}(0.5)$.

As the organic binder, a vehicle prepared by dissolving an ordinarily known ethylcellulose using terpineol or trimethyl pentadiol in monoisobutylate as a solvent was used. The vehicle is usually passed through three rollers twice to five times for homogeneous dispersion. The viscosity of the paste was determined to 15 to 20 Fcps (by rotary viscometer, 10 rpm, at 25°C), which was suitable to screen printing. The obtained copper paste was printed on 88% alumina substrate with a screen printing plate of from 200 mesh to 325 mesh, dried

at 120°C for 15 min., and then fired in an N₂ atmosphere at O₂ concentration of from 4 to 8 ppm at 900°C for 10 min. The evaluation for the quality of the thick film Cu conductor after firing was carried out with regard to the following content.

I. Initial characteristics

a) Surface appearance

○ : Copper glossiness was imparted on all the surface

△ : A portion was discolored by oxidation

× : all the surface was discolored by oxidation

b) Sheet resistance:

Actually measured values (mΩ/□) by L.C.R meter, manufactured by YGP.

c) Solder wettability:

80Pb/40Sn solder, at 240±5°C, 5 sec dipping, flux:

SA-100 available from TAMURA KAKEN Co.

d) Adhesion strength:

A soft copper wire of 0.8φ was soldered to a conductor, the copper wire was bent vertically, and then tensile test was carried out.

III. Reliability Test

a) Refire characteristics (firing three times at 900°C, for 10 min in N₂ atmosphere)

b) Leaving at high-temperature of 150°C for 200 hours

c) Cryogenic cycle test

d) PCT test

Those compositions and the results of the measurements are shown in Table 1. In the table, comparative examples are also described. As apparent from the table, the compositions according to the invention are excellent in solder wettability, adhesion strength with a conductor and in surface appearance.

Table 1

Composition, characteristics		1	2	3	4	5	6	7	8	9
A	Cu powder	88	85	82	85	85	84	84	87	83
	Glass powder	1	2.5	2	2	3	5	0.5	3	4
	Oxide, nonoxide	Cu ₂ O:2.8 V ₂ O ₅ :0.1	FeO:1.0 V ₂ O ₅ :0.5	Cr:0.5 Cu ₂ O:2.5	V ₂ O ₅ :0.1 Bi ₂ O ₃ :2.8	CeO ₂ :1 NiO:1	SnO:0.05 MnO:0.05	Cu ₂ O:2.5 Bi ₂ O ₃ :1.5	ZrB ₂ :0.1 Sb ₂ O ₃ :0.01	SiC:0.01 V ₂ O ₅ :0.101
	Vehicle	8	11	14	10	10	11	12	10	13
B	Surface appearance	○	○	○	○	○	○	△	○	○
	Sheet resistance (m/Ω□)	2.0	2.1	2.2	2.2	2.1	2.3	2.2	2.1	2.2
	Solder wettability(%)	100	90	90	100	80	90	90	100	100
	Adhesion strength kg/2 mm□	2.9	3.0	3.1	3.0	2.8	2.8	2.5	3.1	2.8
C	Surface appearance	○	○	○	○	○	△	△	○	○
	Sheet resistance (m/Ω□)	2.2	2.2	2.4	2.3	2.4	2.8	2.5	1.2	2.
	Solder wettability(%)	80	80	80	90	90	80	70	80	90
	Adhesion strength (kg/2mm□)	2.7	2.8	2.8	2.7	2.8	2.4	2.4	2.9	2.7
Adhesion strength (kg/2mm□) after high-temperature leaving		2.8	2.8	2.8	2.5	2.5	2.4	2.3	2.7	2.8
Adhesion strength (kg/2mm□) after cryogenic cycles		2.3	2.5	2.8	2.2	2.2	2.2	2.1	2.5	2.3
Adhesion strength (kg/2mm□) after PCT		2.1	2.1	2.2	2.0	2.1	2.0	2.0	2.2	2.1

A: Composition/constitution (wt%)

B: Initial characteristics

C: Characteristics after refiring